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(54) Improvements in and relating to the dyeing of cellulose fibres

(57) Cellulosic fibres, and especially fabrics comprising cellulosic fibres, are treated in a bath containing, in addition to one or more micro-dispersed vat dyes, a swelling agent for the cellulosic fibre, followed by the necessary reduction and re-oxidation treatment. It is found that the presence of the swelling agent, suitably one of a range of defined water-soluble polyoxyethylene glycols, improves the penetration of the dye and the uniformity of dyeing. This is especially the case where the cold process is used, that is, where the treatment in the reduction bath and any subsequent storage (e.g. of the wrapped roll of fabric after passing in the alkaline reduction bath) are effected without external application of heat. An alkaline reduction padding bath containing defined amounts of dextrin, sodium silicate and ammonia is recommended to enhance further the uniformity of the dyeing; in particular the incorporation of ammonia is found to promote the evolution of heat in the storage phase of the cold process.

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SPECIFICATION

Improvements in and relating to the dyeing of cellulose fibres

The present invention concerns a process for dyeing cellulose fibres with vat dyes, using swelling agents for swelling the fibres themselves, especially a cold process, the world "cold" signifying the lack of any substantial external application of heat during the reduction stage of the vat dye.

It is well known to use vat-dyes in the dyeing of cellulosic fibres. The use of such dyes has in general entailed a sequence of rather complex operations. Since the dye in its ordinary form does not dye cellulosic fibres, it must first be reduced to the leuco form which allows the dye to penetrate and permeate the cellulosic fibres. Then there is required a re-oxidization of the dye to its normal, oxidized form which imparts to the fibres the desired colouring.

The reduction phase of the dye has traditionally been carried out in a suitable vat by adding to a suspension the dye caustic soda and hydrosulphite (reducing agent) at a temperature of 40°–50°C; the material was then dyed in the bath for a suitable length of time. Thereupon, the material was removed from the bath and the dye that has penetrated the fibre was oxidized by access of air or by application of aqueous hydrogen peroxide.

This method is at present outdated following the availability of vat dyes in a micro-dispersed form, permitting the impregnation of the material to be dyed (in particular, fabrics) with vat dye dispersions and subsequent reduction of the dye *in situ*.

Particularly important are those continuous or semi-continuous techniques that involve the impregnation of the cellulosic fibre with a dispersion of the microfined dye by means of a padding operation, followed by the optional drying of the fibre, then the reduction of the dye deposited on the fibre by reaction with aqueous sodium hydrosulphite and caustic soda in suitable equipment (such as jiggers) in a semi-continuous process, or a further padding in a reducing bath consisting of an aqueous solution of sodium hydrosulphite and caustic soda and subsequent steaming for a few minutes, in a continuous process.

Both the described techniques require an external application of heat, more for the purpose of accelerating the penetration and distribution of the reduced form of the dye in the fibre than for the dye reduction process itself, which is exothermic.

A dyeing process has been attempted, comprising an initial deposition of the dye on the fibre by passing of an aqueous dye dispersion, followed by an optional drying step, and then the passing of the treated fabric in a chemical reducing bath with a high concentration of caustic soda and sodium hydrosulphite, the impregnated fabric being rolled up and left to soak for some hours, taking care that the roll of fabric thus formed is isolated as much as possible from the oxidizing action of the air.

Since the padding of the fabric with the chemical reducing bath occurs in the cold, this process may be considered a semi-continuous cold process. However, it shows numerous drawbacks from the point of view of the characteristics of the finished product. In fact, it does not yield colours of a medium-to-high tinctorial depth, it gives poorly penetrated articles (in comparison with other techniques), and it very often shows selvedge effects.

It has now surprisingly been found that by using in the dye dispersion padding bath a swelling substance for cellulose fibres, even in the cold state or at temperatures not greater than 120°C, the above-described drawbacks are greatly mitigated or eliminated, in particular achieving tinctorial yields that are much higher than those obtained with the cold method just described, and which are in line with those provided by "hot" techniques. Such use of swelling agents also affords very high penetration and uniform spread of the dye in the fibre better than obtainable, in general, with previous techniques and the elimination of the selvedge effect, thanks also to the various expedients which will be set out in the following description.

It has also surprisingly been found that there is a substantial exotherm that occurs in the roll of fabric when the dye has previously been padded together with the swelling agent.

Of particular utility for this latter purpose is the addition to the chemical reduction bath (which may essentially consist of an aqueous solution of cautic soda and hydrosulphite) of 5–30 parts by weight of 18° Bé ammonia per 1000 parts by weight of the bath. The ammonia unexpectedly facilitates the development of heat in the roll.

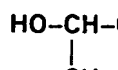
The hydrosoluble swelling agents, of particular effectiveness, belong to the class of polyoxyethyleneglycols of the general formula:

$$R(O-\underset{\displaystyle C_nH_{2n+1}}{\underset{|}{CH}}-CH_2-)_mR_1$$

wherein:

n is 0 or 1;

m is a positive integer;
R is H, a linear or branched alkyl radical having from 1 to 8 carbon atoms,



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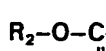
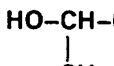
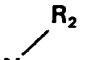


wherein R_2 is a linear or branched alkyl group having from 1 to 8 carbon atoms; and
R_1 is a linear or branched alkyl radical having from 1 to 8 carbon atoms,



OH, OR_2, NHR_2,



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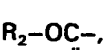

wherein R_2 is as previously defined.

These swelling agents have been found to be particularly effective when applied in a quantity of 40–120 parts by weight for 1000 parts by weight of padding bath containing the dye.

As regards the above-mentioned selvedge effect, this may be minimized by mechanical isolation action of the roll from the surroundings and also by the use of a chemical reduction bath containing caustic soda of 36° Bé, in a quantity of from 80–160 parts by weight for 1000 parts by weight of bath, 18° Bé ammonia in a quantity of 5–30 parts, 5–30 parts of dextrin, aqueous sodium silicate of 40° Bé in a quantity of 5–40 parts and optionally glucose in a quantity of 0–10 parts.

The process of the invention may be practised with conventional vat dyes and may be applied to cellulose fibres of any type. It may also be used for the dyeing of the cellulosic components of blends containing such fibres.

The following is a description of a general procedure which has been found suitable for carrying out the process of the invention.

In 1000 parts by weight of water there are dispersed a suitable quantity of vat dye in a microfined form, 40–120 parts of a swelling agent as previously described, 10–20 parts of sodium alginate (or a suitable amount of another anti-migration agent and/or a synthetic thickener compatible with the dispersing system); the dispersion thus prepared forms the bath in which the cellulose fibre fabric is padded. After impregnation, the fabric is squeezed between two opposed cylinders (mangle rollers) developing a squeezing ratio of 60%–120% (with respect to the weight of the fibre). Thereafter, the material may be dried in hot air and/or by infrared irradiation for times varying from 20 to 120 seconds, at temperatures of 80°–120°C.

The fabric is then padded in a reduction bath consisting of 80–160 parts by weight of caustic soda at 36° Bé, 60–140 parts of sodium hydrosulphite, 5–40 parts of 40° Bé sodium silicate, 5–30 parts of dextrin, 0–10 parts of glucose, and 5–30 parts of 18° Bé ammonia, this mixture being brought up to make 1000 parts by the addition of water. After impregnation, the fabric is again mangled with a squeezing ratio of 80–200%, taking care to wind the fabric properly so that at the end of the operation it will form a roll. This roll should be isolated promptly from the surroundings for instance by wrapping it up in polyethylene sheeting.

The roll is kept, optionally under rotation, for 1–4 hours; thereupon the material is unrolled and subjected to a series of operations of washing and oxidation, optionally using aqueous solutions of hydrogen peroxide, and then to a further series of washings, hot soaping, further rinsings and then drying in accordance with the methods already known to those skilled in the art.

The following examples illustrate how the invention may be carried into effect.

EXAMPLE 1

A padding bath (A) is prepared having the composition:

Bright Green Romantrene FFB (C.I. Vat Green 1)	20 g
Polyoxyethylenglycol with m.wt. about 200	80 g
Sodium alginate in aqueous solution at 2.5% concentration by weight	50 g
Water to make	1 kg

(ROMANTRENE is a Registered Trade Mark)

In this bath was treated a cotton gabardine, followed by mangling, applying a squeezing ratio of 78%. The material was then dried for 80 seconds at 100°C and rolled up.

Separately there was prepared a chemical reduction bath (B) of the following formulation:

caustic soda, 36° Bé	120 g
sodium hydrosulphite	100 g
sodium silicate, 40° Bé	20 g
dextrin	10 g
glucose	5 g
ammonia, 18° Bé	20 g
Water to make	1 kg

With this bath the fabric, already soaked with dye and dried, was padded and then mangled with a squeezing ratio of 100%.

The material from the mangle was then wound to a roll, and the roll was covered with some covering textile material impregnated with the above-described bath (B), and finally wrapped and sealed in a polyethylene sheet.

The roll of fabric was then kept revolving for 120 minutes, after which it was unrolled and re-oxidized, washed soaped and rinsed as indicated in the foregoing general description.

There was obtained a bright green dyeing with a very high penetration free of selvedge effect.

Similar tests carried out either formulating a padding bath (A) free of swelling agent or a bath (B) free of sodium silicate, dextrin and ammonia, gave a less satisfactory result, although still materially better than if the recited components were absent from each bath.

EXAMPLE 2

A light cotton fabric was impregnated with a padding bath similar to bath (A) of example 1, in which, however, there was used the following mixture of dyes:

Oliva Romantrene FT (C.I. Vat Black 25)	27 g/kg
Yellow Romantrene F 3RT (C.I. Vat Yellow 3)	3 g/kg
Brown Romantrene FBR (C.I. Vat Brown 1)	3 g/kg

(ROMANTRENE is a Registered Trade Mark.)

The material was then dried at 120°C for 60 seconds and was then impregnated with a chemical bath similar to bath (B) of example 1 but omitting the glucose. The fabric was squeezed in a mangle with a squeezing ratio of 120%, after which it was wound up and allowed to rest for 180 minutes. There then followed the usual operations of oxidation and finishing.

There was obtained an olive shade for military supplies, with a high yield and penetration.

EXAMPLE 3

A padding bath was prepared consisting of:

Yellow Romantrene GCN (C.I. Vat Yellow 2)	20 g
1-methyl-polyoxyethylengiycol of molecular weight 150	100 g
2.5% w/w aqueous sodium alginate	50 g
water to make	1 kg

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Some heavy cotton fabric was padded and mangled with a squeezing ratio of 70%. This fabric was then dried for 120 seconds at 90°C and then was padded in a chemical bath consisting of:

36° Bé caustic soda	140 g
sodium hydrosulphite	120 g
sodium silicate at 40° Bé	25 g
dextrin	10 g
ammonia at 18° Bé	10 g
water to make	1 kg

The padded fabric was mangled at a squeezing ratio of 80%, rolled up and covered up with a polyethylene film, keeping the roll revolving slowly for 4 hours. There was obtained a dyeing of very high penetration and free of any fault.

The yield was superior to that obtainable with the known cold-rolling methods and slightly inferior (by 10–20%) with respect to a developing process by vaporization.

EXAMPLE 4

A padding bath was prepared which contained:

Blue Romantrene (RTM) BC (C.I. Vat Blue 6)	30 g
Polyoxyethylenglycol of mwt. 250	70 g
2.5% w/w aqueous sodium alginate	50 g
water to make	1 kg

A cotton fabric was padded in this bath and then mangled with a squeezing ratio of 100%, followed by drying at 120°C for 80 seconds.

Separately there was prepared a chemical bath consisting of:

36° Bé caustic soda	100 g
Sodium hydrosulphite	80 g
Sodium silicate at 40° Bé	25 g
Dextrin	5 g
18° Bé ammonia	15 g
water to make	1 kg

The fabric was then padded in this bath and mangled with a squeezing ratio of 140% and was then rolled up. The resulting roll was wrapped and kept in storage for 3 hours. There was obtained a fabric dyed in a bright blue of an excellent quality level.

EXAMPLE 5

There was prepared a padding bath containing the following components:

Brown Romantrene (R.T.M.) FR (C.I. Vat Brown 3)	30 g
Polyoxyethylenglycol of mwt. 200	100 g
2.5% w/w aqueous sodium alginate	50 g
water to make	1 kg

A cotton fabric was padded and mangled with a squeezing ratio of 60%.

The fabric thus padded, was further padded in a bath consisting of:

Brown Romantrene (R.T.M.) FR	3 g
36° Bé caustic soda	110 g
Sodium hydrosulphite	90 g
Sodium silicate	15 g
dextrin	10 g
18° Bé ammonia	20 g/kg
water to make	1 kg

The impregnated fabric was mangled with a squeezing ratio of 100%, rolled up, wrapped in a polyethylene sheet, and kept revolving for 150 minutes. Thereafter there were carried out the usual oxidation and finishing operations, to yield a brown of good depth and penetration.

EXAMPLE 6

A mixed fabric of polyester/cotton, with a weight ratio of the two fibres of 65:35 was padded in a bath consisting of:

Red Tersetile SL (C.I. Dispersed Red 72)	4.5 g
Ruby Tersetile RL (C.I. Dispersed Red 73)	2.6 g
Red Romantene (RTM) FBB (C.I. Vat Red 10)	12.5 g
Polyoxyethylenglycol of m.wt. 400	40 g
2.5% w/w aqueous sodium alginate	60 g
water to make	1 kg

(TERSETILE is a Registered Trade Mark.)

The squeezing ratio was 70%. The fabric was dried at 120°C for 80 seconds and then thermofixed at 210°C for 60 seconds. This latter operation allows the dispersed dye to be fixed on the polyester fibre. The fabric was then padded in a bath consisting of:

caustic soda at 36° Bé	100 g
sodium hydrosulphite	60 g
sodium silicate at 40° Bé	20 g
dextrin	5 g
ammonia of 18° Bé strength	10 g
water to make	1 kg

The squeezing ratio used was 100%.

The fabric thus padded was rolled up, covered with a polyethylene film and stored for 3 hours. After this period the material was subjected to the usual finishing operations. There was obtained a dyeing of a good uniformity of shade between the two fibres, an excellent penetration and a good yield.

In the examples both the first padding, in the dye dispersion bath, and the second padding, in the chemical reduction bath, were carried out at room temperature, namely 20–25°C.

CLAIMS

1. A process for the dyeing of cellulosic fibres in which the material to be dyed is padded in an aqueous bath comprising one or more vat dyes followed by padding in an alkaline reduction bath comprising sodium hydrosulphite, in which the first padding is conducted in the presence of a substance effective to swell the cellulosic fibres.
2. A process according to claim 1 applied to the dyeing of mixed cellulosic/synthetic fibres.
3. A process according to claim 2 in which the mixed fibres, padded in the vat dye bath, are treated to fix the dye to the synthetic fibre prior to transference to the alkaline reduction bath.
4. A process according to claim 1, 2 or 3 in which the swelling substance is a water-soluble ether of the general formula:

$$R(O-\underset{\displaystyle C_nH_{2n+1}}{\underset{|}{CH}}-CH_2)_mR_1$$

wherein n, m, R and R_1 are as hereinbefore defined.

5. A process according to any foregoing claim in which the swelling substance is present in the first padding bath in an amount by weight of 40–120 parts per 1000 parts of bath.
6. A process according to any foregoing claim in which the first padding bath contains a thickening and/or anti-migration substance.
7. A process according to any foregoing claim in which the fibres, after removal from the alkaline reduction bath, are stored in a still-damp condition for a substantial time prior to working-up by oxidative and washing treatment.
8. A process according to claim 7 in which the fibres are in the form of a fabric and the still-damp fabric is stored as a roll.
9. A process according to claim 8 in which the roll is wrapped to prevent substantial access of air and localised drying.
10. A process according to claim 7, 8 or 9 in which the alkaline reduction bath contains ammonia in an amount sufficient to establish generation of heat within the stored fibres.
11. A process according to any of the foregoing claims in which the alkaline reduction bath comprises by weight, in addition to caustic soda and sodium hydrosulphite, 5–30 parts of dextrin-type starchy material, 0–10 parts of a sugar, 5–40 parts of 40° Bé sodium silicate and 5–30 parts of 18° Bé ammonia per 1000 parts of the bath.
12. A process according to any of the foregoing claims in which the treatment of the fibres in the alkaline reduction bath, and any subsequent storage of the still-damp fibres are carried out without external application of heat.
13. A process according to claim 1, substantially as set forth in any of the foregoing

examples.

14. Fibres when dyed by a process as set forth in any of the foregoing claims.

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